

# Epoxy Resins

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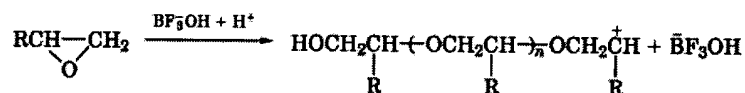
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## 4. Curing Reactions

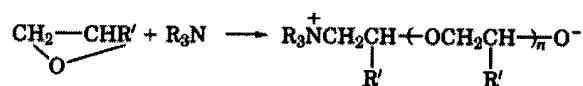
A variety of reagents has been described for converting the liquid and solid epoxy resins to the cured state, which is necessary for the development of the inherent properties of the resins. Liquid epoxy resins contain mainly epoxy groups and solid resins are composed of both epoxy and hydroxyl curing sites. The curing agents or hardeners are categorized as either catalytic or coreactive and the functional groups of the resins are terminal epoxy together with a pendent hydroxyl per repeat unit of the polymer chain.

Catalytic curing agents initiate resin homopolymerization, either cationic or anionic, as a consequence of using a Lewis acid or base in the curing process. The Lewis acid catalysts frequently employed are complexes of boron trifluoride with amines or ethers.



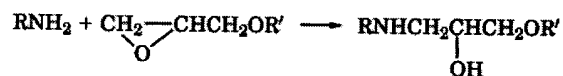
Mechanisms for polymerization of epoxides by Lewis acids are proposed in References (11–15).

The most important Lewis bases are tertiary amines or polyamines converted into tertiary amines upon reaction with epoxide groups.



Mechanisms for reaction of tertiary amines with epoxides are discussed in References 16 and 17.

Coreactive curing agents are polyfunctional reagents that are employed in stoichiometric quantities with epoxy resins and possess active hydrogen atoms. The important classes include polyamines, polyamides (formed from polyamines and dimerized fatty acids), polyphenols, polymeric thiols, polycarboxylic acids, and anhydrides. Polyamines constitute a large class of hardeners with aliphatic, aromatic, cycloaliphatic, and heterocyclic groups. Cure of liquid epoxy resins is readily accomplished via the epoxy groups at room temperature with nonaromatic amines and at slightly elevated temperatures with aromatic amines, although reaction of the latter can be accelerated to function at RT. The mechanism of the reaction between epoxy resins and primary aliphatic amines is discussed in detail in References (18–23). The overall curing reaction may be depicted as follows:





Detailed discussions of network formation from amines and epoxy resins are provided in References 24 and 25.

Polyamides provide RT cure of epoxy-terminated resins as well as flexibilization; they are derived by reaction of dimerized vegetable oil fatty acids (dimer acids) with polyamines.

Comparisons of the properties of solvent-free liquid coatings based on unmodified bisphenol A epoxies cured with varying amine hardeners are shown in Table 6. Examples include diethylenetriamine [111-40-0],  $\text{H}_2\text{NC}_2\text{H}_4\text{NHC}_2\text{H}_4\text{NH}_2$  (7), triethylenetetramine [112-24-3],  $\text{H}_2\text{NC}_2\text{H}_4\text{NHC}_2\text{H}_4\text{NHC}_2\text{H}_4\text{NH}_2$  (8), *N*-(2-hydroxyethyl)diethylenetriamine [1965-29-3] (9), and *N,N'*-di(2-hydroxyethyl)diethylenetriamine [4484-60-0].



(9)



(10)

For solvent-based ambient cure systems polyamides are often the hardeners of choice. For heat-cured systems, anhydrides are used to provide higher heat-resistance systems but at the expense of flexibility.

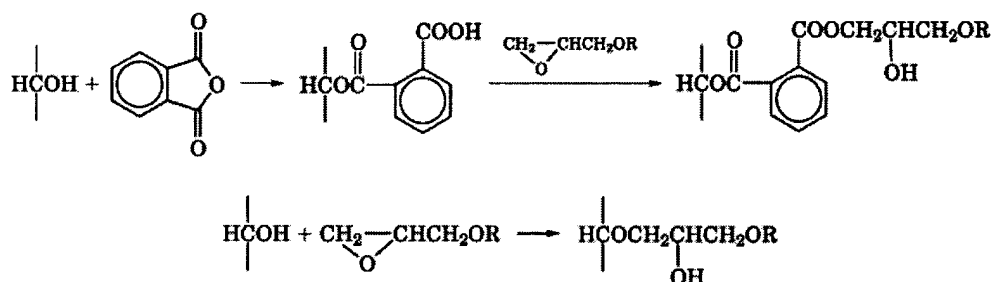
**Table 6. Comparative Properties of Bisphenol A–Epoxy Resins Cured with Different Hardener**

Properties	Short-chain aliphatic polyamine	Oxyalkylated short-chain polyamine	Long-chain polyamine adduct	Aromatic polyamine adduct	Polyanhydride
chemical structure	(7), (8)	(9), (10)	trimethyl-1,6-hexanediamine [25620-58-0]		reaction product of polyamine with dimeric acids
advantages	low viscosity, generally good chemical resistance	low viscosity, generally good chemical resistance, low toxicity	color stability, generally good chemical resistance, good flexibility	long pot life, good acid resistance, cures in presence of moisture	long pot life, general good solvent resistance, good flexibility and adhesion
limitations	dermatitis potential, poor organic acid resistance, mixing ratio critical, film appearance	short pot life, poor organic acid resistance	short pot life, low organic acid resistance	high viscosity, color, low resistance to aromatic solvents	poor organic acid resistance, blushing
application-handling	100:10 or 13	100:25	100:35	100:60	100:40
mixing ratio by wt					
viscosity, mPa · s (= cP)	4,500	3,000	7,800	8,000	>10,000
pot life, min	30–60	<30	23	135	75
color, Gardner	1–4	5–8	1–2	>12	6
dry time (paper-free), h	1.5–3	<10	ca 2	ca 16	
film quality					
flow	poor	poor	good	good	good
surface blushing	blushing	blushing	blush-resistant	blush-resistant	blush-resistant
color stability	good	good	good	poor	fair

<sup>a</sup> Bais: resin = diglycidyl ether of bisphenol A (wt per epoxide (WPE) = 182 – 196).

Polyphenols or phenol-terminated resins are utilized to effect chemical cross-linking of epoxy resins with added catalysts or accelerators for the reaction (26).

The reactions of carboxylic acids and anhydrides with epoxy resins have been extensively studied in a variety of investigations, particularly References (27–31). The general reaction of epoxide resins and anhydrides is



Typical epoxy–anhydride systems are described in Table 7.

**Table 7. Epoxy–Anhydride System Handling and Performance**

Anhydride name	CAS Registry Number	Melting point or viscosity at 25°C	Mol wt	Recommended concentration, phr <sup>a</sup>	Curing cycles
phthalic anhydride	[84-44-9]	131°C	148	30–75	4 to 24 h at 150°C
methyl-4-endomethylene-tetrahydrophthalic anhydride	[129-64-6]	175–275 mPa · s <sup>b</sup>	178	80–90	2 h at 140°C + 2 – 192 h at 200°C
hexahydrophthalic anhydride	[85-42-7]	35–37°C	154	50–100	2 h at 100°C, or 2 h at 100°C + 2 h at 149°C
tetrahydrophthalic anhydride	[85-43-8]	99–101°C	152	70–80	2 h at 100°C + 4 h

					at 150°C
					2 h at 121°C
					or 1 h at 100°C
		290 mPa			+ 2 h
dodecenylsuccinic anhydride	[25377-73-5]	$\cdot s^b$	266	130–150	at 204°C

<sup>a</sup> phr = Parts per hundred parts of resin.

<sup>b</sup> mPa  $\cdot$  s = cP.

Epoxy resins contain both epoxy terminal groups and pendent hydroxyl groups and are cured in accordance with available sites present in a given resin. Low and intermediate weight resins respond to curing by reagents such as dicyandiamide (see CYANAMIDES) and imidazoles at elevated temperatures. The curing reactions of these reagents are discussed in References (32–36).

Cross-linking with aminoplasts and phenoplasts constitutes an important class of hardeners for high molecular-weight epoxy resins that require elevated temperature cures (see AMINO RESINS).

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(prior art suggested proportional balancing to achieve desired results in the formation of alloy).

### III. REBUTTAL OF *PRIMA FACIE* CASE OF OBVIOUSNESS

Applicants can rebut a *prima facie* case of obviousness based on overlapping ranges by showing the criticality of the claimed range. "The law is replete with cases in which the difference between the claimed invention and the prior art is some range or other variable within the claims. . . . In such a situation, the applicant must show that the particular range is critical, generally by showing that the claimed range achieves unexpected results relative to the prior art range." *In re Woodruff*, 919 F.2d 1575, 16 USPQ2d 1934 (Fed. Cir. 1990). See MPEP § 716.02 - § 716.02(g) for a discussion of criticality and unexpected results.

A *prima facie* case of obviousness may also be rebutted by showing that the art, in any material respect, teaches away from the claimed invention. *In re Geisler*, 116 F.3d 1465, 1471, 43 USPQ2d 1362, 1366 (Fed. Cir. 1997) (Applicant argued that the prior art taught away from use of a protective layer for a reflective article having a thickness within the claimed range of "50 to 100 Angstroms." Specifically, a patent to Zehender, which was relied upon to reject applicant's claim, included a statement that the thickness of the protective layer "should be not less than about [100 Angstroms]." The court held that the patent did not teach away from the claimed invention. "Zehender suggests that there are benefits to be derived from keeping the protective layer as thin as possible, consistent with achieving adequate protection. A thinner coating reduces light absorption and minimizes manufacturing time and expense. Thus, while Zehender expresses a preference for a thicker protective layer of 200-300 Angstroms, at the same time it provides the motivation for one of ordinary skill in the art to focus on thickness levels at the bottom of Zehender's suitable range- about 100 Angstroms- and to explore thickness levels below that range. The statement in Zehender that [i]n general, the thickness of the protective layer should be not less than about [100 Angstroms]' falls far short of the kind of teaching that would discourage one of skill in the art from fabricating a protective layer of 100 Angstroms or less. [W]e are therefore not convinced that there was a sufficient teaching away in the art to overcome [the] strong case of obviousness' made out by Zehender."). See MPEP § 2145, paragraph X.D., for a discussion of "teaching away" references.

#### 2144.06 Art Recognized Equivalence for the Same Purpose

### COMBINING EQUIVALENTS KNOWN FOR THE SAME PURPOSE

"It is *prima facie* obvious to combine two compositions each of which is taught by the prior art to be useful for the same purpose, in order to form a third composition to be used for the very same purpose.... [T]he idea of combining them flows logically from their having been individually taught in the prior art." *In re Kerkhoven*, 626 F.2d 846, 850, 205 USPQ 1069, 1072 (CCPA 1980) (citations omitted) (Claims to a process of preparing a spray-dried detergent by mixing together two conventional spray-dried detergents were held to be *prima facie* obvious.). See also *In re Crockett*, 279 F.2d 274, 126 USPQ 186 (CCPA 1960) (Claims directed to a method and material for treating cast iron using a mixture comprising calcium carbide and magnesium oxide were held unpatentable over prior art disclosures that the aforementioned components individually promote the formation of a nodular structure in cast iron.); and *Ex parte Quadranti*, 25 USPQ2d 1071 (Bd. Pat. App. & Inter. 1992) (mixture of two known herbicides held *prima facie* obvious). But see *In re Geiger*, 815 F.2d 686, 2 USPQ2d 1276 (Fed. Cir. 1987) ("Based upon the prior art and the fact that each of the three components of the composition used in the claimed method is conventionally employed in the art for treating cooling water systems, the board held that it would have been *prima*

*facie* obvious, within the meaning of 35 U.S.C. 103, to employ these components in combination for their known functions and to optimize the amount of each additive.... Appellant argues... hindsight reconstruction or at best,... obvious to try'.... We agree with appellant.”).

### **SUBSTITUTING EQUIVALENTS KNOWN FOR THE SAME PURPOSE**

In order to rely on equivalence as a rationale supporting an obviousness rejection, the equivalency must be recognized in the prior art, and cannot be based on applicant's disclosure or the mere fact that the components at issue are functional or mechanical equivalents. *In re Ruff*, 256 F.2d 590, 118 USPQ 340 (CCPA 1958) (The mere fact that components are claimed as members of a Markush group cannot be relied upon to establish the equivalency of these components. However, an applicant's expressed recognition of an art-recognized or obvious equivalent may be used to refute an argument that such equivalency does not exist.); *In re Scott*, 323 F.2d 1016, 139 USPQ 297 (CCPA 1963) (Claims were drawn to a hollow fiberglass shaft for archery and a process for the production thereof where the shaft differed from the prior art in the use of a paper tube as the core of the shaft as compared with the light wood or hardened foamed resin core of the prior art. The Board found the claimed invention would have been obvious, reasoning that the prior art foam core is the functional and mechanical equivalent of the claimed paper core. The court reversed, holding that components which are functionally or mechanically equivalent are not necessarily obvious in view of one another, and in this case, the use of a light wood or hardened foam resin core does not fairly suggest the use of a paper core.); *Smith v. Hayashi*, 209 USPQ 754 (Bd. of Pat. Inter. 1980) (The mere fact that phthalocyanine and selenium function as equivalent photoconductors in the claimed environment was not sufficient to establish that one would have been obvious over the other. However, there was evidence that both phthalocyanine and selenium were known photoconductors in the art of electrophotography. “This, in our view, presents strong evidence of obviousness in substituting one for the other in an electrophotographic environment as a photoconductor.” 209 USPQ at 759.).

An express suggestion to substitute one equivalent component or process for another is not necessary to render such substitution obvious. *In re Fout*, 675 F.2d 297, 213 USPQ 532 (CCPA 1982).

#### **2144.07 Art Recognized Suitability for an Intended Purpose**

The selection of a known material based on its suitability for its intended use supported a *prima facie* obviousness determination in *Sinclair & Carroll Co. v. Interchemical Corp.*, 325 U.S. 327, 65 USPQ 297 (1945) (Claims to a printing ink comprising a solvent having the vapor pressure characteristics of butyl carbitol so that the ink would not dry at room temperature but would dry quickly upon heating were held invalid over a reference teaching a printing ink made with a different solvent that was nonvolatile at room temperature but highly volatile when heated in view of an article which taught the desired boiling point and vapor pressure characteristics of a solvent for printing inks and a catalog teaching the boiling point and vapor pressure characteristics of butyl carbitol. “Reading a list and selecting a known compound to meet known requirements is no more ingenious than selecting the last piece to put in the last opening in a jig-saw puzzle.” 325 U.S. at 335, 65 USPQ at 301.).

See also *In re Leshin*, 227 F.2d 197, 125 USPQ 416 (CCPA 1960) (selection of a known plastic to make a container of a type made of plastics prior to the invention was held to be obvious); *Ryco, Inc. v. Ag-Bag Corp.*, 857 F.2d 1418, 8 USPQ2d 1323 (Fed. Cir. 1988) (Claimed agricultural bagging machine, which differed from a prior art machine only in that the brake means were hydraulically operated rather than mechanically operated, was held to be obvious over the prior art machine in view of references which disclosed hydraulic brakes for performing the same function, albeit in a